



# Accurately substituting Fe for Ni<sub>2</sub> atom in Ni-MOF with defect-rich for efficient oxygen evolution reaction: Electronic reconfiguration and mechanistic study

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## ABSTRACT

Designing metal-organic framework (MOF) with controllable lattice defects and oxygen vacancies is of great significance for effective oxygen evolution reaction (OER). We achieved controlled lattice defects and generated oxygen vacancies in the Ni-MOF nanoflowers by accurately substituting Fe atoms for Ni<sub>2</sub> atoms. The optimized Ni<sub>0.67</sub>Fe<sub>0.33</sub>-MOF/CFP exhibits remarkable OER performance (an ultra-low overpotential of 281 mV at 100 mA cm<sup>-2</sup> and a Tafel slope of 38 mV dec<sup>-1</sup>) and excellent stability (the activity maintains for 80 h at 100 mA cm<sup>-2</sup>). Importantly, it is revealed that the active species is the Ni<sub>0.67</sub>Fe<sub>0.33</sub>-MOF/NiFeOOH complex for OER. Density functional theory (DFT) provides the insightful catalytic mechanism that the Fe atoms and oxygen vacancies are critical in optimizing the *d*-band center and promoting the dissociation of oxygen-containing intermediates. Our work introduces a strategy for designing defect-rich MOF-based electrocatalysts, opening up new possibilities for efficient OER systems.

## 1. Introduction

The oxygen evolution reaction (OER) plays a vital role in various electrochemical energy storage and conversion technologies [1–3]. However, the OER process, which involves the formation of O–O bonds and a four-proton-coupled electron transfer, often exhibit sluggish kinetics [4–6]. OER kinetics are determined by the rate-determining step (RDS), i.e. the adsorption and desorption of intermediates on the active site [7]; the efficiency of this step is related to the *d*-orbital electronic structure of the active site [8]. Therefore, it is effective to improve the electrochemical performance of electrode materials by tuning the electronic structure of the active site of the electrochemical reaction at the atomic scale. Transition metal-organic frameworks (MOFs) have gained considerable attention in recent years due to their well-dispersed metal sites, uniform pores, and tunable electronic structures [9–11]. However, the limited number of exposed electrochemically active sites and the dense structures of MOFs hinder the formation of active sites, resulting in unsatisfactory electrochemical performance [12].

To overcome these limitations, the concept of introducing subtle defects into nanostructures has emerged, such as multi-metal engineering [13,14], lattice defect engineering [15], and oxygen defect engineering [16]. Among these strategies, lattice defect engineering is a crucial approach for optimizing the electronic structure of nanomaterials. Introducing surface and bulk defects through defect engineering can alter atomic and lattice distances [17], thereby influencing the geometrical shape and electronic structure of active sites [18,19], ultimately optimizing the electrocatalytic activity of materials [20]. Previous studies, conducted by Yao et al., induced lattice distortion and dislocations through the electrocatalytic process, resulting in the redistribution of electron density in specific regions and promoting charge and ion transfer [17]. However, the lattice defects generated in these studies were randomly formed during the preparation process. Hence, a controllable approach to inducing lattice defects and establishing the relationship between microstructural lattice defects and active surface sites in MOF remains a significant challenge. Oxygen defect engineering, on the other hand, has shown potential in enhancing the electronic

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conductivity of transition metal catalysts [21], modifying surface adsorption of intermediates, and altering the electronic structure to facilitate charge transfer [22]. Various methods, such as heat treatment, reduction treatment, and plasma etching, have been used to induce a large number of defects under non-equilibrium conditions [23]. For instance, Luo et al. introduced abundant oxygen vacancies into CeO<sub>2</sub> through a high-temperature calcination strategy, which optimized intermediate adsorption/dissociation and improved charge transfer [24]. However, the time-consuming and complex preparation process of oxygen-defective materials has hindered their widespread application and promotion. Thus, there is a need to find an effective and convenient approach to induce oxygen vacancies in electrode materials.

Motivated by these concepts, we have developed a mild and effective strategy to prepare defective Ni<sub>0.67</sub>Fe<sub>0.33</sub>-MOF nanoflowers. As expected, the catalyst we prepared exhibits excellent OER activity by adjusting the degree of lattice and oxygen vacancies through the precise substitution of Fe atoms for the Ni2 site in Ni-MOF. Density functional theory (DFT) calculations further validate that the introduction of Fe and the presence of oxygen vacancies can effectively regulate the electron structure and spin state density of the highly active Ni site, balance the adsorption/desorption of intermediates, and minimize the energy barrier of OER. As a result, the intrinsic activity of the catalyst is improved.

## 2. Experimental section

### 2.1. Surface modification of the CFP

Prior to the synthesis, the CFP (cut as 1 cm × 2 cm in size) was added to a 25 mL Teflon-lined stainless steel autoclave containing HNO<sub>3</sub> (68 wt %) and maintained at 120 °C for 4 h. Subsequently, the CFP was washed several times with a mixture of water and ethanol until a neutral pH was obtained. Finally, the prepared CFP was stored in an ethanol solution for future use.

### 2.2. Synthesis of Ni<sub>1-x</sub>Fe<sub>x</sub>-MOF/CFP

0.4 mmol Ni(NO<sub>3</sub>)<sub>2</sub>·6 H<sub>2</sub>O, 0.1 mmol Fe(NO<sub>3</sub>)<sub>3</sub>·9 H<sub>2</sub>O and 0.5 mmol Thiophene-2,5-dicarboxylic acid (H<sub>2</sub>TDC) were dissolved in a combination of 6 mL N,N-Dimethylformamide (DMF) and water. The above solution and pre-treated CFP were then transferred into a 25 mL Teflon-lined stainless steel autoclave and heated at 120 °C for 12 h. After cooling to room temperature, the resulting product was washed more than five times with a mixture of water and ethanol to remove impurities. After a 12 h drying period, the resulting brownish-yellow sample has been designated as Ni<sub>0.67</sub>Fe<sub>0.33</sub>-MOF/CFP, in accordance with the true Ni and Fe ratio. By varying the proportion of Ni(NO<sub>3</sub>)<sub>2</sub>·6 H<sub>2</sub>O to Fe(NO<sub>3</sub>)<sub>3</sub>·9 H<sub>2</sub>O, we successfully synthesized Ni-MOF/CFP, Ni<sub>0.80</sub>Fe<sub>0.20</sub>-MOF/CFP, Ni<sub>0.21</sub>Fe<sub>0.79</sub>-MOF/CFP and Fe<sub>2</sub>O<sub>3</sub>/CFP. The loading of the resulting catalyst on the CFP was about 4.25 mg.

### 2.3. Synthesis of Ni<sub>1-x</sub>Fe<sub>x</sub>-MOF

The synthesis of Ni<sub>1-x</sub>Fe<sub>x</sub>-MOF powder catalysts followed a similar method to that of Ni<sub>1-x</sub>Fe<sub>x</sub>-MOF/CFP, except that the CFP was not added into the Teflon liner.

## 3. Results and discussion

### 3.1. Synthesis and characterizations

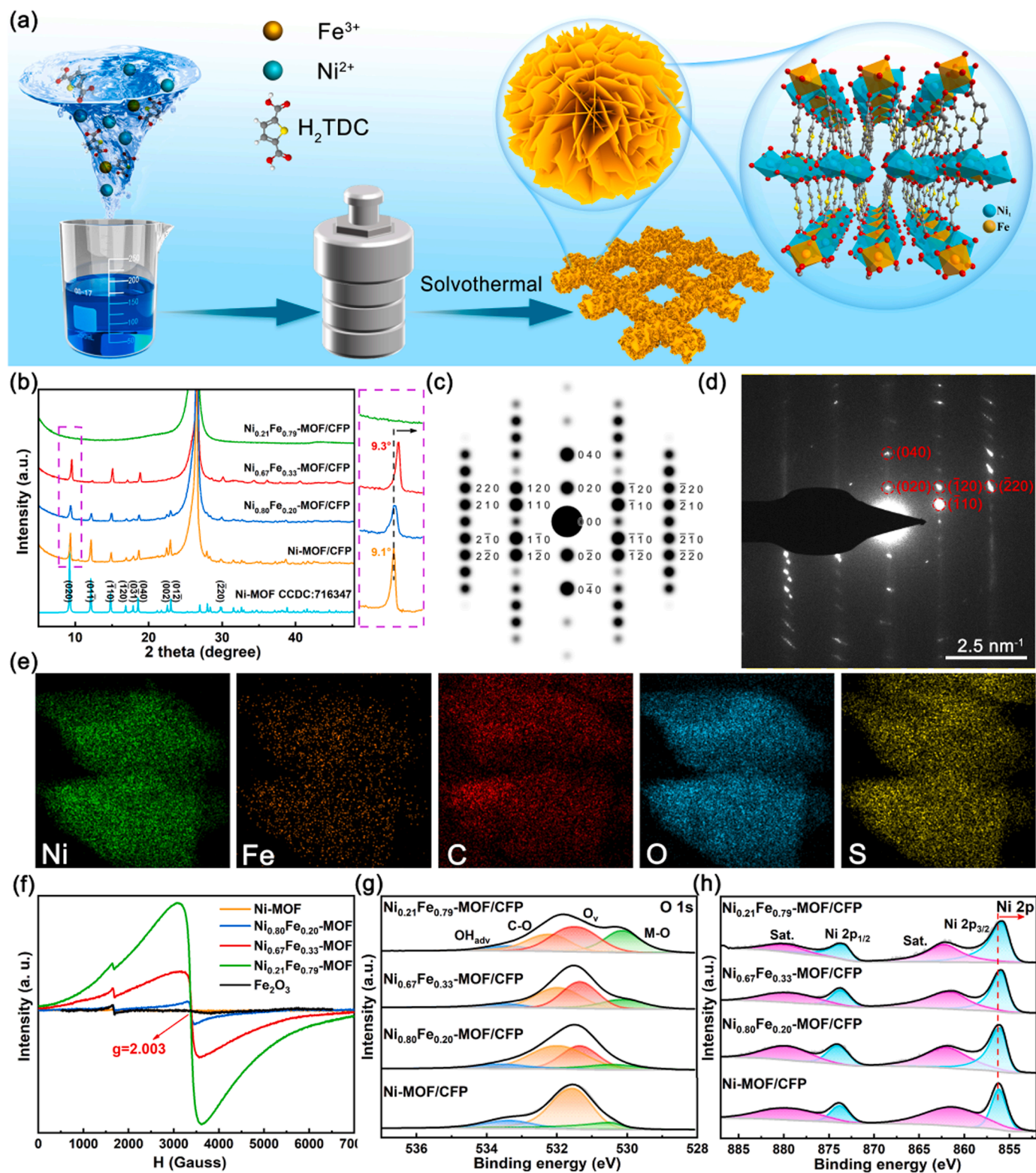
According to Fig. 1a, the synthesis of Ni<sub>0.67</sub>Fe<sub>0.33</sub>-MOF nanoflowers on CFP was achieved through a one-step hydrothermal method, utilizing H<sub>2</sub>TDC as a ligand and Fe(NO<sub>3</sub>)<sub>3</sub>·9 H<sub>2</sub>O and Ni(NO<sub>3</sub>)<sub>2</sub>·6 H<sub>2</sub>O as metal sources. To determine the crystal structure and atomic arrangement, X-ray diffraction (XRD) analysis was performed on the synthesized

samples. As shown in Fig. 1b, the characteristic diffraction peaks of the Ni-MOF material matched well with the theoretical XRD simulation results (CCDC: 716347) [25], indicating the high crystallinity of Ni-MOF and facilitating the preparation of highly crystalline Ni<sub>1-x</sub>Fe<sub>x</sub>-MOF/CFP. The XRD characterization confirmed the well-defined atomic structure of Ni-MOF. Additional details of the ligand TDC<sup>2-</sup> and its coordination modes are presented in Fig. S1, where the TDC<sup>2-</sup> ligand exhibited an asymmetric tetradentate (κ<sup>1</sup>-κ<sup>1</sup>)-(κ<sup>1</sup>-κ<sup>1</sup>)-μ<sub>4</sub> coordination mode. The compound formed a three-dimensional framework by bridging a chain of repeating structural units [Ni1O<sub>6</sub>]<sub>2</sub>[Ni2O<sub>6</sub>] parallel to the *a*-axis with the two-dentate ligand TDC<sup>2-</sup>. The coordination of Ni atoms in this framework involved octahedral coordination in two ways: (1) Ni1 atom coordination included two μ<sub>3</sub>-OH, two oxygen atoms in water molecules, and two ligand oxygen atoms; (2) Ni2 atom coordination included two μ<sub>3</sub>-OH and four oxygen atoms from different ligands.

To gain a deeper understanding of the crystal structure of Ni-MOF, the corresponding powder was also subjected to XRD analysis. As depicted in Fig. S2a, the diffraction peaks of in-situ grown Ni-MOF/CFP were similar to those of powdered Ni-MOF, with no noticeable impurity peaks, indicating that they possessed the same crystal structure. High strength peaks at 26° can be attributed to the carbon fiber substrate [26]. Upon the introduction of Fe into Ni-MOF, the diffraction peak of Ni-MOF at 9.1° experienced a slight shift towards a higher angle (9.3°). This transformation can be attributed to the fact that the ionic radius of Fe<sup>3+</sup> (0.064 nm) is much smaller than that of Ni<sup>2+</sup> (0.072 nm). When Fe replaces Ni in Ni-MOF, the crystal plane spacing shrinks and lattice distortion occurs, which causes the diffraction peak to shift higher [27].

The introduction of Fe atoms in Ni-MOF plays a crucial role in regulating the degree of grain surface defects. As the Fe atom concentration rises, there's a marked decline in the diffraction peak intensities associated with the (01 $\bar{1}$ ), (0 $\bar{3}$ 1), (002) and (01 $\bar{2}$ ) crystal facets. Intriguingly, by the time the Ni/Fe ratio reaches 4, these peaks are almost non-existent, as evidenced in Fig. 1b. Notably, analysis of the MOF structure reveals that these lattice faces are composed of a point lattice of Ni2 atoms in the MOF structure, indicating that Fe atom doping can accurately replace Ni2 atoms, leading to the destruction of the corresponding lattice faces (Fig. S2b). The substitution mechanism is shown in Fig. S3. Consequently, the degree of lattice defects increases with the increasing proportion of Fe atoms replacing Ni2 atoms. When the Ni/Fe ratio is 1, the characteristic diffraction peaks of Ni-MOF completely disappear and exhibit low crystallinity. This suggests that a significant number of Fe atoms further replace Ni1 atoms after the directional substitution of Ni2 atoms, resulting in the disruption of the original ordered structure of Ni-MOF and the generation of numerous lattice defects. Interestingly, XRD analysis reveals that when only single-metal Fe is present, the crystal surface diffraction peaks correspond well with Fe<sub>2</sub>O<sub>3</sub> (PDF# 89-0599) (Fig. S4). This indicates that Fe atoms cannot actively coordinate with the ligand to form MOF but can accurately replace Ni2 atoms in Ni-MOF, supporting the previous inference. The Ni/Fe metal atom ratio in Ni<sub>1-x</sub>Fe<sub>x</sub>-MOF was further analyzed by ICP-MS (Table S1), and the results showed that the Ni/Fe metal atom ratio in Ni<sub>0.67</sub>Fe<sub>0.33</sub>-MOF/CFP is approximately 2, which is consistent with the conjecture that Fe atom completely replaces Ni2 atomic position.

Raman spectroscopy was further utilized to attest to the successful synthesis of bimetallic Ni<sub>1-x</sub>Fe<sub>x</sub>-MOF/CFP (Fig. S2c). The characteristic peaks observed in the Raman spectrum of Ni<sub>0.67</sub>Fe<sub>0.33</sub>-MOF/CFP correspond to those of previously reported NiFe-MOF [28]. Specifically, the peak located at 1470 cm<sup>-1</sup> can be attributed to the stretching vibration of ν(COO<sup>-</sup>) [29], while the stretching vibration of ν(C-O), resulting from the deprotonation of hydroxyl groups after coordination, is observed at 1134 cm<sup>-1</sup>. Additionally, the peaks at 811 cm<sup>-1</sup>, 688 cm<sup>-1</sup>, and 562 cm<sup>-1</sup> correspond to the bending vibrations of the C-H bond in the thiophene five-membered ring, the bending vibration of the C-S bond, and the vibration of the M-O bond, respectively [30,31]. Importantly,



**Fig. 1.** Design strategy, morphology, and structural characterizations of  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$  nanoflowers. (a) Schematic illustration of the synthesis of  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$  nanoflowers, (b) XRD patterns of  $\text{Ni}_{0.21}\text{Fe}_{0.79}\text{-MOF/CFP}$ ,  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$ ,  $\text{Ni}_{0.80}\text{Fe}_{0.20}\text{-MOF/CFP}$ ,  $\text{Ni-MOF/CFP}$  and simulated data from the reported crystal structure, (c) projection along [001] axial SAED model, (d) experimental SAED pattern of  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$ , and (e) corresponding elemental mapping images of  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$ . (f) EPR spectra of  $\text{Ni-MOF}$ ,  $\text{Ni}_{0.80}\text{Fe}_{0.20}\text{-MOF}$ ,  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF}$ ,  $\text{Ni}_{0.21}\text{Fe}_{0.79}\text{-MOF}$  and  $\text{Fe}_2\text{O}_3$ . High-resolution O 1s (g) and Ni 2p (h) XPS spectra of  $\text{Ni-MOF/CFP}$ ,  $\text{Ni}_{0.80}\text{Fe}_{0.20}\text{-MOF/CFP}$ ,  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$  and  $\text{Ni}_{0.21}\text{Fe}_{0.79}\text{-MOF/CFP}$ .



the hypo crystallization caused by the massive doping of Fe to induce lattice defects does not affect the change in the MOF phase.

Morphological and structural analysis of  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$  was performed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM image (Fig. S5a) reveals that  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$  has a 3D nanoflower morphology, consisting of 1D nanosheets with an average thickness of about 160 nm (Fig. S5b and Fig. S6). This unique structure provides a larger available surface area and superior mass transfer rates compared to disordered and stacked structures. The selected area electron diffraction (SAED) map (Fig. 1d) of  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$  matches well with the simulated results along the crystal structure's band axis (001) (Fig. 1c), confirming its excellent crystallographic properties. Strong Bragg reflection points of (020), (040), ( $\bar{1}10$ ), ( $\bar{1}20$ ) and ( $\bar{2}20$ ) can be clearly observed, indicating the ultra-high crystallinity of  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF}$ . Energy dispersive X-ray spectroscopy (EDX) elemental mapping images reveal that Ni, Fe, C, O, and S are uniformly distributed on the surface of  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$  (Fig. 1e). Additionally, the morphology and microstructure of Ni-MOF/CFP were investigated for comparison. SEM and TEM characterization revealed a rod-shaped morphology for Ni-MOF/CFP with a diameter of approximately 1  $\mu\text{m}$  (Fig. S7a-b). SAED images (Fig. S7c) confirmed the high crystallinity of Ni-MOF/CFP, consistent with the results of  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$ , thereby indicating the identical crystal structure of both materials, which aligns with the XRD analysis. The high-resolution transmission electron microscopy (HRTEM) image presented in Fig. S8a reveals lattice fringes corresponding to the (020) crystal planes of Ni-MOF-MOF/CFP, exhibiting a spacing of 0.95 nm. Notably, the HRTEM image of  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$  (Fig. S8b) displays regions with undulating lattice streaks. These distorted streaks can likely be traced back to the lattice defects stemming from Fe atom doping into Ni-MOF, an observation that aligns with prior literature findings [32]. Such induced lattice defects could potentially unveil more active sites, subsequently enhancing the OER reaction's efficiency [15]. Furthermore, EDX analysis shows a uniform distribution of Ni, C, O, and S elements in Ni-MOF/CFP (Fig. S7d). The morphology of the comparison samples  $\text{Ni}_{0.80}\text{Fe}_{0.20}\text{-MOF/CFP}$ ,  $\text{Ni}_{0.21}\text{Fe}_{0.79}\text{-MOF/CFP}$  and  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF}$  powders is shown in Fig. S9. It can be seen that the morphology of  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF}$  powder is similar to that of  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$ . Furthermore, the morphology of  $\text{Ni}_{0.80}\text{Fe}_{0.20}\text{-MOF/CFP}$  can be perceived as intermediate between Ni-MOF/CFP and  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$ . It should be noted that the MOF in  $\text{Ni}_{0.21}\text{Fe}_{0.79}\text{-MOF/CFP}$  is in a low crystalline state due to the increase in the proportion of Fe atoms, leading to the disruption of the morphology.

Electron paramagnetic resonance (EPR) characterization was employed to investigate the activated O on the  $\text{Ni}_{1-x}\text{Fe}_x\text{-MOF}$  surface. As viewed in Fig. 1f, no EPR signal is observed in Ni-MOF and  $\text{Fe}_2\text{O}_3$ , while bimetallic MOF exhibits an obvious EPR signal with  $g = 2.003$ , indicating that the introduction of Fe induces the formation of O defects, consistent with the results of O 1 s analysis in XPS [33]. Interestingly, the enhancement of the EPR signal aligns with the increasing Fe doping ratio, namely  $\text{Ni}_{0.21}\text{Fe}_{0.79}\text{-MOF} > \text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF} > \text{Ni}_{0.80}\text{Fe}_{0.20}\text{-MOF} > \text{Ni-MOF}$ .

X-ray photoelectron spectroscopy (XPS) was utilized to investigate the chemical composition and elemental valence states of  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$  before and after OER testing. It is worth mentioning that the binding energies were calibrated using the C 1 s peak at 284.8 eV [34]. The XPS survey spectrum of  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$  confirms the presence of Ni, Fe, C, O, and S (Fig. S10), indicating the successful incorporation of Fe. As seen in Fig. 1g, the high-resolution O 1 s spectrum of Ni-MOF/CFP shows characteristic peaks at 530.5 eV, 531.6 eV and 533.3 eV, which are attributed to metal-oxygen (M-O) bond, C-O bond and adsorbed water ( $\text{H}_2\text{O}_{\text{ads}}$ ), respectively [17]. In the high-resolution O 1 s spectrum of  $\text{Ni}_{0.80}\text{Fe}_{0.20}\text{-MOF/CFP}$ ,  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$  and  $\text{Ni}_{0.21}\text{Fe}_{0.79}\text{-MOF/CFP}$ , peaks at specific energies 530.0 eV, 531.3 eV, 532.0 eV, and 533.0 eV correspond to the M-O bond, oxygen vacancies

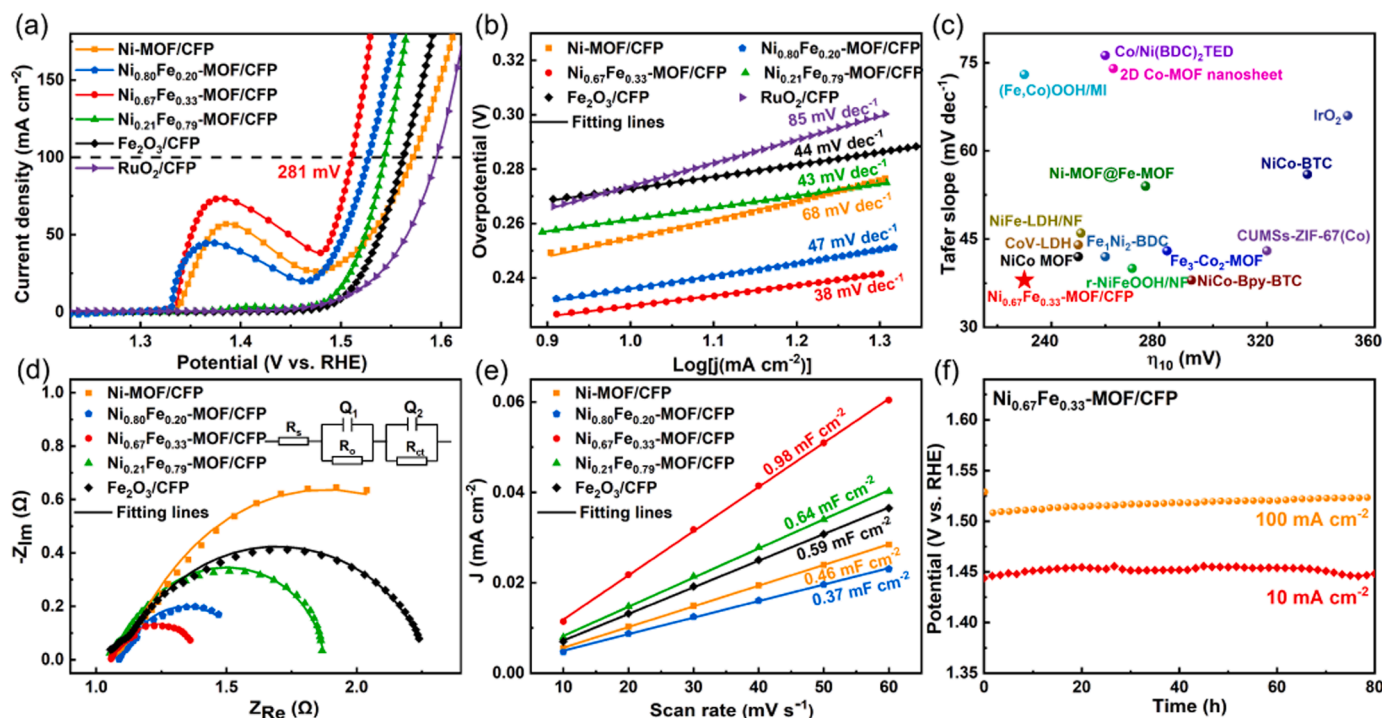
( $\text{O}_v$ ), C-O bond, and adsorbed  $\text{H}_2\text{O}$  ( $\text{H}_2\text{O}_{\text{ads}}$ ), respectively [35,36]. The introduction of lattice defects via Fe doping leads to the creation of these oxygen vacancies in Ni-MOF. Such a modification has a consequential impact on the coordination environment and the electronic framework of the O atoms. Specifically, it causes a drop in the binding energy of the M-O bond and an elevation in the binding energy of the C-O bond [37–39]. The change in the M-O bond binding energy suggests that the lattice defects activated lattice oxygen and generated oxygen vacancies, which are beneficial for the catalytic reaction [20]. Notably, the  $\text{O}_v$  peak intensities in the O 1 s spectra exhibit a gradual increase with the rise in Fe atomic substitution, accompanied by a concurrent increase in M-O bond peak intensities. This phenomenon likely stems from the fact that Fe substitution disrupts the ligand oxygen in the Ni-MOF, leading to the formation of additional Fe-O bonds. Moreover, the results were confirmed by the fact that only  $\text{Fe}_2\text{O}_3$  was generated by using iron salts during the process of the catalyst preparation.

The Ni 2p high-resolution XPS spectrum of  $\text{Ni}_{0.80}\text{Fe}_{0.20}\text{-MOF/CFP}$ ,  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$  and  $\text{Ni}_{0.21}\text{Fe}_{0.79}\text{-MOF/CFP}$  (Fig. 1h) was deconvoluted into Ni 2p<sub>3/2</sub> (855.9 eV), Ni 2p<sub>1/2</sub> (873.7 eV) and two satellite peaks, indicating the presence of  $\text{Ni}^{2+}$  [19,40,41]. Notably, compared with Ni-MOF/CFP, the Ni 2p peak of  $\text{Ni}_{1-x}\text{Fe}_x\text{-MOF/CFP}$  will be shifted to the lower energy level step by step as the proportion of Fe atoms increases, suggesting that the lattice defects induced by Fe substitution can modulate the electronic structure of the active Ni center [42]. Besides, the Fe 2p spectrum of  $\text{Ni}_{0.80}\text{Fe}_{0.20}\text{-MOF/CFP}$ ,  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$  and  $\text{Ni}_{0.21}\text{Fe}_{0.79}\text{-MOF/CFP}$  manifests that the peaks located at 711.0 eV and 724.2 eV are assigned to 2p<sub>3/2</sub> and 2p<sub>1/2</sub> of  $\text{Fe}^{3+}$ , respectively (Fig. S11) [30]. In summary, the introduction of lattice defects by Fe atom doping in Ni-MOF/CFP results in the formation of oxygen vacancies. This in turn impacts the electronic structures of both Ni and Fe atoms, leading to shifts in the binding energies of Ni 2p and Fe 2p [38]. This shift in energy promotes more efficient electron transfer between metal centers, particularly from Fe to Ni. This suggests a more pronounced electronic interaction between Ni and Fe, allowing for a greater number of electrons to populate the Ni's  $e_g$  orbital. However, due to the stronger overlap between the  $e_g$  orbitals involved in  $\sigma$ -bonding and the oxygen-related adsorbate compared to the  $t_{2g}$  orbitals involved in  $\pi$ -bonding, they can more directly facilitate the electron transfer between the surface cation and the adsorbate intermediate in catalytic reactions [43]. Such dynamics considerably hasten the adsorption/desorption cycles of oxygen-rich species like  $\text{OH}^*$ ,  $\text{OOH}$ , and O, thereby amplifying the OER activity [44].

### 3.2. Electrocatalytic OER activities

A series of catalysts were evaluated for their OER performance in 1.0 M KOH using a typical three-electrode system. Based on the linear sweep voltammetry (LSV) curves that were calibrated to the reversible hydrogen electrode (RHE) and resistance ( $iR$ ) corrected (Fig. 2a),  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$  exhibits the lowest overpotential of 281 mV at 100  $\text{mA cm}^{-2}$ , significantly superior to that of Ni-MOF/CFP,  $\text{Ni}_{0.80}\text{Fe}_{0.20}\text{-MOF/CFP}$ ,  $\text{Ni}_{0.21}\text{Fe}_{0.79}\text{-MOF/CFP}$ ,  $\text{Fe}_2\text{O}_3\text{/CFP}$  and  $\text{RuO}_2\text{/CFP}$ . Owing to the presence of an oxidation peak in  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$ , the reverse LSV test was performed, yielding an overpotential of only 230 mV at 10  $\text{mA cm}^{-2}$  (Fig. S12). Notably, both  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$  and Ni-MOF/CFP exhibit an anodic oxidation peak, which can be attributed to the oxidation of  $\text{Ni}^{2+}$  to  $\text{Ni}^{3+/4+}$  and deprotonation of hydroxyl groups, confirming the surface reconstruction of MOF into hydroxides [45,46]. Additionally, the Tafel slope is an important indicator to evaluate the OER reaction kinetics. The Tafel slopes were calculated from the reverse LSV data of  $\text{Ni}_{1-x}\text{Fe}_x\text{-MOF/CFP}$  catalysts. As described in Fig. 2b, The Tafel slope value (38  $\text{mV dec}^{-1}$ ) of  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$  is smaller than that of Ni-MOF/CFP (68  $\text{mV dec}^{-1}$ ),  $\text{Ni}_{0.80}\text{Fe}_{0.20}\text{-MOF/CFP}$  (43  $\text{mV dec}^{-1}$ ),  $\text{Ni}_{0.21}\text{Fe}_{0.79}\text{-MOF/CFP}$  (47  $\text{mV dec}^{-1}$ ),  $\text{Fe}_2\text{O}_3\text{/CFP}$  (44  $\text{mV dec}^{-1}$ ) and  $\text{RuO}_2\text{/CFP}$  (85  $\text{mV dec}^{-1}$ ), confirming that  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$  exhibits the most effective catalytic kinetics.





**Fig. 2.** Electrochemical OER tests in 1.0 M KOH electrolyte using a three-electrode system for Ni-MOF/CFP,  $\text{Ni}_{0.80}\text{Fe}_{0.20}$ -MOF/CFP,  $\text{Ni}_{0.67}\text{Fe}_{0.33}$ -MOF/CFP,  $\text{Ni}_{0.21}\text{Fe}_{0.79}$ -MOF/CFP,  $\text{Fe}_2\text{O}_3$ /CFP and  $\text{RuO}_2$ /CFP. (a) LSV polarization curves, (b) Tafel slopes, (c) comparison of the overpotential at  $100 \text{ mA cm}^{-2}$  and Tafel slope with previously reported catalysts, (d) double-layer capacitance ( $C_{dl}$ ) plots, (e) Nyquist plots and (f) chronopotentiometry of  $\text{Ni}_{0.67}\text{Fe}_{0.33}$ -MOF/CFP at 10 and  $100 \text{ mA cm}^{-2}$ .

However, the OER electrocatalytic trend is slightly different from the EPR trend. This can be attributed to the beneficial effect of appropriate O vacancies, which help tune the electronic structure and intermediates of metal compounds [20,47], and provide additional active sites for the material, thereby reducing the overpotential required for the reaction [48,49]. Among them,  $\text{Ni}_{0.67}\text{Fe}_{0.33}$ -MOF/CFP showcases a higher concentration of oxygen vacancies relative to both Ni-MOF/CFP and  $\text{Ni}_{0.80}\text{Fe}_{0.20}$ -MOF/CFP. Compared to the low-crystalline structure of  $\text{Ni}_{0.21}\text{Fe}_{0.79}$ -MOF/CFP,  $\text{Ni}_{0.67}\text{Fe}_{0.33}$ -MOF/CFP retains the structure of MOF due to the appropriate lattice defects. Therefore,  $\text{Ni}_{0.67}\text{Fe}_{0.33}$ -MOF/CFP exhibits the highest electrochemical activity due to the combined effect of oxygen vacancies and lattice defects.

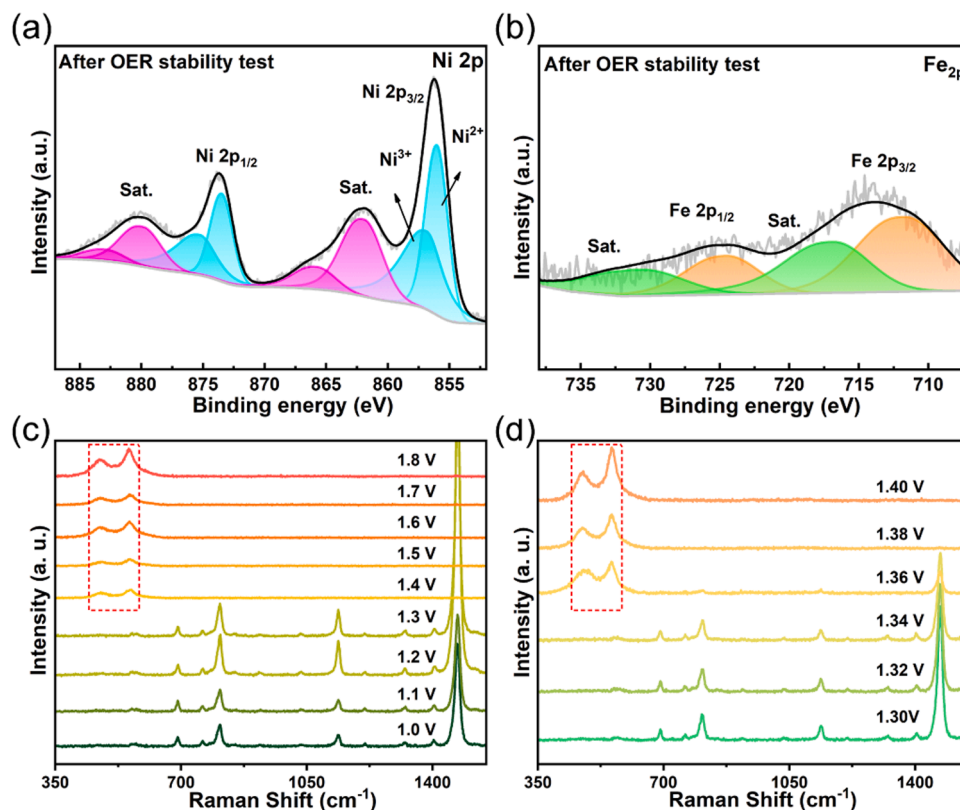
It is noteworthy that the overpotential ( $\eta_{10}$ ) and Tafel slope of  $\text{Ni}_{0.67}\text{Fe}_{0.33}$ -MOF/CFP are significantly lower than those of other excellent OER catalysts reported recently (Fig. 2c). To further understand the catalytic kinetics of OER process, electrochemical impedance spectroscopy (EIS) was performed. As viewed in Fig. 2d,  $\text{Ni}_{0.67}\text{Fe}_{0.33}$ -MOF/CFP displays a smaller semicircle diameter than Ni-MOF/CFP,  $\text{Ni}_{0.80}\text{Fe}_{0.20}$ -MOF/CFP,  $\text{Ni}_{0.21}\text{Fe}_{0.79}$ -MOF/CFP and  $\text{Fe}_2\text{O}_3$ /CFP, demonstrating faster charge transfer and better electrical conductivity of  $\text{Ni}_{0.67}\text{Fe}_{0.33}$ -MOF/CFP. The electrochemical active surface area (ECSA) of the samples was assessed by measuring the double-layer capacitance ( $C_{dl}$ ) to understand the source of the remarkable OER activity (Fig. S13 and Fig. 2e).  $\text{Ni}_{0.67}\text{Fe}_{0.33}$ -MOF/CFP exhibited the highest  $C_{dl}$  ( $0.98 \text{ mF cm}^{-2}$ ), indicating a maximal specific surface area and the exposure of more active sites. Meanwhile, the intrinsic catalytic prowess of the catalysts was assessed through the computation of the turnover frequency (TOF), leveraging the results from ICP-MS (Table S1). Notably, the TOF value for  $\text{Ni}_{0.67}\text{Fe}_{0.33}$ -MOF/CFP overshadowed those of other catalysts at an equivalent potential, underscoring its exceptional OER conversion efficiency and potent intrinsic catalytic activity [50]. From the standpoint of mass-specific activity,  $\text{Ni}_{0.67}\text{Fe}_{0.33}$ -MOF/CFP stood out remarkably. At an overpotential of 300 mV, it boasted mass current densities that were triple and quadruple those of Ni-MOF/CFP and

$\text{Fe}_2\text{O}_3$ /CFP, respectively (refer to Fig. S14b). Additionally, long-term stability is an essential criterion for evaluating the practical application value of electrocatalysts. Remarkably,  $\text{Ni}_{0.67}\text{Fe}_{0.33}$ -MOF/CFP demonstrated extraordinary OER stability with no significant potential change at 10 and  $100 \text{ mA cm}^{-2}$  over 80 h (Fig. 2f).

### 3.3. Analyzing the dynamic transformation of catalysts during the OER process

After OER test, the Ni 2p high-resolution XPS spectrum of  $\text{Ni}_{0.67}\text{Fe}_{0.33}$ -MOF/CFP is indexed to Ni  $2p_{3/2}$  (855.6 eV) and Ni  $2p_{1/2}$  (873.5 eV) of  $\text{Ni}^{2+}$ , Ni  $2p_{3/2}$  (856.8 eV) and Ni  $2p_{1/2}$  (875.3 eV) of  $\text{Ni}^{3+}$ , and corresponding satellite peaks (Fig. 3a). Importantly, the Ni 2p peak shifts towards higher binding energy by 0.17 eV after OER testing, indicating that high-valence  $\text{Ni}^{3+}/\text{Ni}^{4+}$  is formed on the surface of  $\text{Ni}_{0.67}\text{Fe}_{0.33}$ -MOF/CFP after OER, which facilitates efficient and rapid electron transfer during OER [51]. In addition, the Fe 2p spectra were shifted towards higher binding energies after the OER test, although no new peaks appeared (Fig. 3b). In the O 1s spectrum, the intensity of the lattice oxygen peak exhibits a decreasing trend after the OER, suggesting that the lattice oxygen obtained through the lattice defect strategy contributes to the catalytic reaction [20]. In summary, these shifts indicate electron transfer between Fe and Ni through the bridging oxygen of the ligand, while oxygen atoms serve as intermediates between various metal atoms to maintain charge balance and strengthen metal-metal interactions.

In addition to the abundant defects, Fe species also play a crucial role in promoting the OER activity of  $\text{Ni}_{0.67}\text{Fe}_{0.33}$ -MOF/CFP. To understand the true catalytic sites and the key role of Fe sites in the catalytic system, a series of characterizations were performed on  $\text{Ni}_{0.67}\text{Fe}_{0.33}$ -MOF/CFP after electrochemical test, including XRD, EPR, XPS, SEM, TEM and electrochemical in situ Raman spectroscopy. As shown in Fig. S15a-b,  $\text{Ni}_{0.67}\text{Fe}_{0.33}$ -MOF/CFP retains nanosheet morphology. The SAED pattern (Fig. S15c) shows diffuse diffraction rings, indicating that the MOF has



**Fig. 3.** High-resolution XPS spectra of  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$  after OER stability test, (a) Ni 2p, and (b) Fe 2p. Electrochemical in situ Raman spectra of (c)  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$  in the potential range of 1.00–1.80 V (vs. RHE) and (d)  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$  in the potential range of 1.30–1.40 V (vs. RHE).

been transformed into a lower crystalline state [52]. Notably, some diffraction rings correspond to those of  $\text{NiFeOOH}$  (PDF# 14-0117), demonstrating that the MOF has been partially transformed into  $\text{NiFeOOH}$ , and  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/NiFeOOH}$  is the true active species of the OER reaction. The post-electrochemical reaction XRD spectra, as illustrated in Fig. S16, reveal that the characteristic MOF peaks are partially preserved. The emergence of additional peaks can be attributed to  $\text{NiFeOOH}$ , further corroborating the aforementioned characterization. As demonstrated in the EPR and high-resolution O 1s spectra (Fig. S17), it is noteworthy that the characteristic peak associated with oxygen vacancies persists even after the electrochemical reaction of  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$ . EDS mapping images manifest a homogeneous distribution of Ni, Fe, C, O and S (Fig. S15d). And the presence of S confirms the retention of MOF.

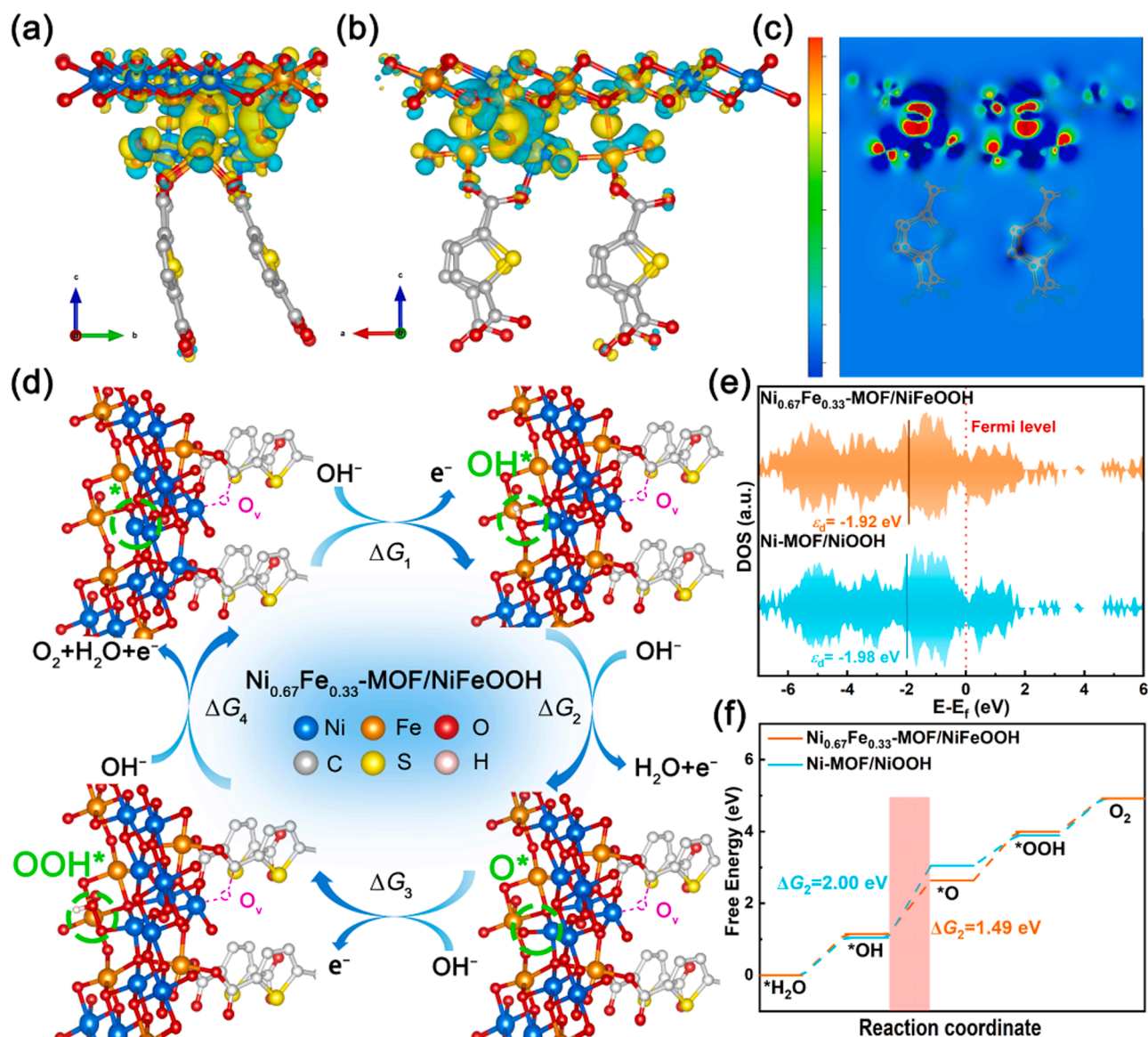
To further understand the surface reconstruction process, electrochemical in situ Raman spectroscopy was employed to analyze the structural transformation of  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$  and  $\text{Ni-MOF/CFP}$  in the potential range of 1.00–1.80 V. As shown in Fig. 3c, no significant changes were observed in Raman features of  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$  at 1.00–1.30 V (vs. RHE), indicating that the Ni species have not undergone oxidation at this stage. However, when the potential reaches 1.40 V (vs. RHE), the Raman characteristic peaks of MOF disappeared, and two distinct signal peaks are detected at  $\sim 474\text{ cm}^{-1}$  and  $554\text{ cm}^{-1}$ , corresponding to the  $\text{E}_g$  bending and  $\text{A}_1 g$  stretching vibrations of Ni/Fe-O in  $\text{NiFeOOH}$  [51,53,54]. The Raman spectra of  $\text{Ni-MOF/CFP}$  exhibit a similar phase transition to  $\text{NiFeOOH}$  in the potential range of 1.30–1.40 V (Fig. S18a).

Further in situ Raman spectra were then investigated in the potential range of 1.30–1.40 V (vs. RHE) at 0.02 V intervals (Fig. 3d and Fig. S18b). At 1.34 V (vs. RHE), the characteristic peaks of  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$  remain unchanged, while those of  $\text{Ni-MOF}$  disappear, indicating that  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$  exhibits better electrocatalytic stability compared to  $\text{Ni-MOF/CFP}$ . Subsequently, when the potential

reaches 1.36 V (vs. RHE), both  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$  and  $\text{Ni-MOF/CFP}$  exhibit characteristic peaks of  $\text{NiOOH}$ . However, the intensity of the  $\text{NiFeOOH}$  characteristic peak in  $\text{Ni-MOF/CFP}$  is weaker than that in  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$ , indicating that the oxidation potential required for the formation of  $\text{NiFeOOH}$  active species is lower for  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$ . This difference can be attributed to the presence of Fe species and oxygen vacancies, which lower the oxidation potential required for the formation of the high-valence active hydroxide species of NiFe [42,53,55]. The coordinated electronic structure of oxygen vacancies further promotes the formation of highly active metal hydroxides by accelerating charge transfer [48,56].

#### 3.4. OER mechanism investigation by DFT theoretical simulation

To elucidate the intrinsic OER catalytic mechanism of the  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/NiFeOOH}$  composite interface, theoretical investigations based on DFT calculations were conducted. Charge density analysis reveals visible charge accumulation at the interface, effectively confirming strong electronic interaction between  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF}$  ( $\text{Ni-MOF}$ ) and  $\text{NiFeOOH}$  ( $\text{NiOOH}$ ) (Fig. 4a-c and Fig. S19) [57]. Notably, compared to  $\text{Ni-MOF/NiOOH}$ , the charge on Ni/Fe atoms in  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/NiFeOOH}$  was found to significantly accumulate on the O atoms, indicating that electrons transfer from Ni/Fe to adjacent O atoms, which is consistent with the XPS results after electrochemistry. This can be attributed to the fact that the defective O atoms in  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/NiFeOOH}$  can accommodate more charges [20]. The transfer of electrons from Ni/Fe to the neighboring O atoms will lead to an increase in the highly valent active sites of Ni/Fe, which effectively promotes the rapid OER-catalyzed reaction [58,59]. Based on the four-step mechanism of adsorbate evolution under alkaline conditions, the optimal models and corresponding geometries of various intermediates of  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/NiFeOOH}$  were shown in Fig. 4d. For comparison, the OER process of  $\text{Ni-MOF/NiOOH}$  was calculated



**Fig. 4.** Differential charge density diagrams of  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/NiFeOOH}$  (a) side view, (b) main view, and (c) 2D dimensional charge density map. Yellow and cyan regions represent charge accumulation and depletion, respectively. (d) OER mechanism illustration of  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/NiFeOOH}$ . (e) The density of state (DOS), and (f) Gibbs free energy diagrams of  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/NiFeOOH}$  and  $\text{Ni-MOF/NiOOH}$ .

(Fig. S20). Furthermore, the density of states (DOS) and  $d$ -band center ( $\epsilon_d$ ) of  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/NiFeOOH}$  and  $\text{Ni-MOF/NiOOH}$  were calculated to gain a deeper understanding of the electronic structure changes in the catalyst. As seen in Fig. 4e,  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/NiFeOOH}$  has enhanced DOS near the Fermi level compared to  $\text{Ni-MOF/NiOOH}$ , indicating that  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/NiFeOOH}$  possesses better conductivity [60,61]. Moreover, the  $\epsilon_d$  of  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/NiFeOOH}$  is  $-1.92\text{ eV}$ , closer to the Fermi level than  $\text{Ni-MOF/NiOOH}$  ( $\epsilon_d = -1.98\text{ eV}$ ), indicating that the introduction of Fe can effectively optimize the electronic structure and  $d$ -band center of Ni sites [42], thereby enhancing the adsorption capacity of the materials to the intermediates [62]. Finally, the activity of metals towards OER was analyzed by calculating the Gibbs free energy. Generally, the step with the largest change in Gibbs free energy ( $\Delta G$ ) in the four-electron transfer steps of alkaline OER is determined as the rate-determining step (RDS) [63]. As shown in Fig. 4f, although the RDS of  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/NiFeOOH}$  and  $\text{Ni-MOF/NiOOH}$  are both the second step ( $\text{*OH} \rightarrow \text{*O}$ ), the  $\Delta G_2$  of  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/NiFeOOH}$  is  $1.49\text{ eV}$  much lower than that of  $\text{Ni-MOF/NiOOH}$  ( $2.00\text{ eV}$ ), which reveals a lower theoretical onset overpotential ( $0.26\text{ V}$ ) and more

favorable OER kinetics of  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/NiFeOOH}$  [35], and the enhanced OER activity of bimetallic  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/NiFeOOH}$  with oxygen vacancies. Therefore, the computational results are consistent with experimental observations.

Charge transfer processes and electronic interactions were also elucidated from the point of view of the electronic structure of the  $d$ -orbital in  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/NiFeOOH}$ . In  $\text{Ni}^{2+}$  ( $t_{2g}^6 e_g^2$ ) and  $\text{Ni}^{3+}$  ( $t_{2g}^6 e_g^1$ ) ions, the  $\pi$ -symmetric ( $t_{2g}$ )  $d$ -orbital are fully occupied, resulting in strong electron-electron repulsive interactions with the bridging oxygen [64]. In contrast, the valence electron configuration of the  $\text{Fe}^{3+}$  ion is ( $t_{2g}^3 e_g^2$ ), which corresponds to a  $\pi$ -symmetric ( $t_{2g}$ )  $d$ -orbital with three unpaired electrons. Therefore, the electronic interaction between the bridging oxygen and  $\text{Fe}^{3+}$  is relatively weak [65]. Compared with  $\text{Ni-MOF/NiOOH}$ , the Ni-O-Fe bond formed by  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/NiFeOOH}$  will lead to electron-electron repulsion between Ni and oxygen enhancing the  $\pi$ -donation energy of Fe-O due to the coupling between  $\text{Ni}^{2+}$  ( $\text{Ni}^{3+}$ ) and  $\text{Fe}^{3+}$ , prompting the electron transfer from Ni to Fe [66]. With the decrease of electron density at the Ni site,  $\text{Ni}^{2+}$  ( $\text{Ni}^{3+}$ ) with low half-full  $e_g$  orbital will form proper binding with adsorbed oxygen,



which will be favorable to improve the catalytic activity of OER and accelerate the reaction rate [67]. In summary, the presence of Fe in  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/NiFeOOH}$  makes  $\text{Ni}^{2+}$  more difficult to oxidize, resulting in  $\text{Ni}^{3+/4+}$  having a stronger oxidizing ability and therefore faster OER kinetics [68,69].

### 3.5. Overall water splitting analysis

Inigorated by the outstanding OER performance of  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$ , a two-electrode system was assembled with  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$  and Pt/C as the respective anode and cathode ( $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}^{(+)} \parallel \text{Pt/C}^{(-)}$ ) to assess the potential of overall water splitting (Fig. 5a). As displayed in Fig. 5b, the  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}^{(+)} \parallel \text{Pt/C}^{(-)}$  electrolyzer requires only 1.48 and 1.71 V to reach current densities of 10 and 200  $\text{mA cm}^{-2}$ , respectively, significantly lower than that of  $\text{RuO}_2^{(+)} \parallel \text{Pt/C}^{(-)}$  (1.53 and 1.92 V for 10 and 200  $\text{mA cm}^{-2}$ ). Additionally, the overall water-splitting performance of  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF}$  surpasses most advanced electrocatalysts reported in the literature (Fig. 5c and Table S3). The electrochemical durability of  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}^{(+)} \parallel \text{Pt/C}^{(-)}$  was further studied via chronoamperometry testing. As illustrated in Fig. 5d,  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}^{(+)} \parallel \text{Pt/C}^{(-)}$  can operate normally for 80 h at current density of 200  $\text{mA cm}^{-2}$ . These results demonstrate that  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$  is a promising non-noble metal alternative with notable stability and excellent activity.

## 4. Conclusions

In summary, we have prepared an efficient and stable  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$  electrocatalyst using a one-step mild solvothermal method. Structural characterization and elemental analysis manifest that the introduction of Fe atoms precisely replaces the Ni2 site in Ni-MOF, triggering controllable lattice defects and generating oxygen vacancies. The optimal  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$  exhibits excellent catalytic activity (281 mV @ 100  $\text{mA cm}^{-2}$ ) and long-term stability

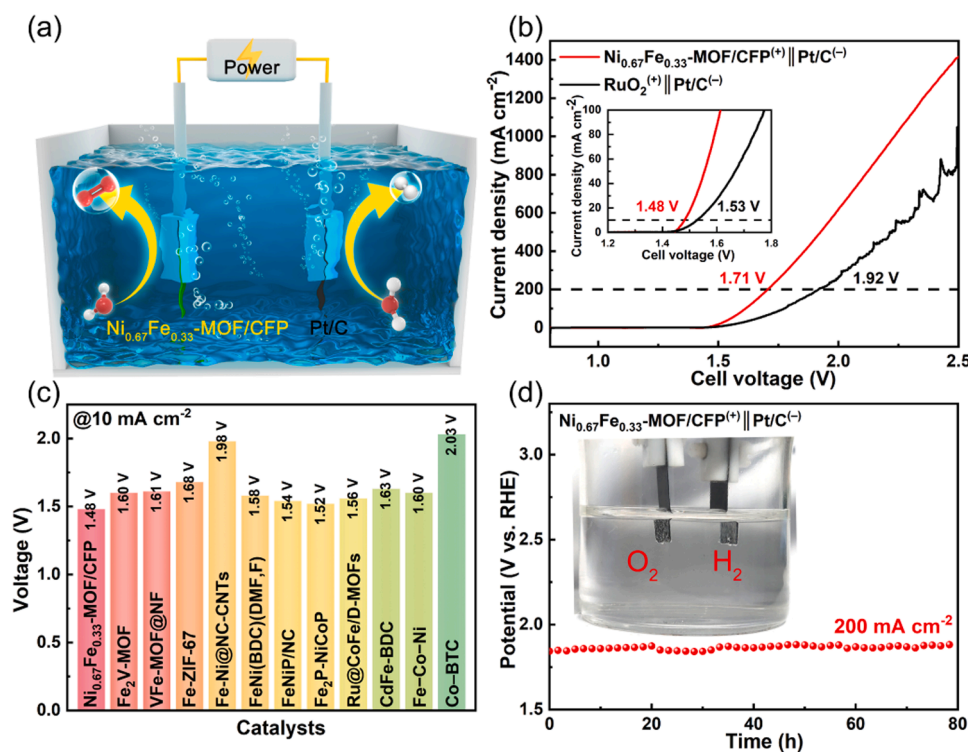
(80 h @ 100  $\text{mA cm}^{-2}$ ) in an alkaline medium. Furthermore, the fabricated  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}^{(+)} \parallel \text{Pt/C}^{(-)}$  just need ultra-low cell voltage of 1.48 and 1.71 V to reach current densities of 10 and 200  $\text{mA cm}^{-2}$ , respectively, superior to those of  $\text{RuO}_2^{(+)} \parallel \text{Pt/C}^{(-)}$ . Meanwhile, the  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}$ -based electrolyzer can operate stably for 80 h at the current density of 200  $\text{mA cm}^{-2}$  without significant attenuation, indicating its good durability. In situ Raman analysis confirms that  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/NiFeOOH}$  is the active species in OER catalysis. Experimental and DFT calculations result prove that the introduction of Fe atoms and the presence of oxygen vacancies in  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/NiFeOOH}$  effectively modify the electronic structure of the Ni site to move the *d*-band center towards the Fermi level, optimize the desorption process of  $^*\text{OH}$  intermediates, and promote the charge transfer process in OER. This work provides a new perspective for introducing multi-defect coordinated unsaturated metal site regulation of MOF as an efficient electrocatalyst.

### CRediT authorship contribution statement

**Shifan Zhang:** Writing – original draft, Investigation, Formal analysis, Methodology. **Zhiyang Huang:** Data curation, Conceptualization. **Tayirjan Taylor Isimjan:** Writing – review & editing. **Dandan Cai:** Supervision, Writing – review & editing, Validation, Funding acquisition. **Xiulin Yang:** Supervision, Writing – review & editing, Funding acquisition.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.



**Fig. 5.** (a) Schematic diagram of overall water splitting in two-electrode system, (b) polarization curves of  $\text{Ni}_{0.67}\text{Fe}_{0.33}\text{-MOF/CFP}^{(+)} \parallel \text{Pt/C}^{(-)}$  and  $\text{RuO}_2^{(+)} \parallel \text{Pt/C}^{(-)}$  for overall water splitting in 1.0 M KOH, (c) comparison the cell voltage at 10  $\text{mA cm}^{-2}$  with previously reported catalysts in 1.0 M KOH, and (d) chronoamperometry test at 200  $\text{mA cm}^{-2}$ .

## Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2023.123448](https://doi.org/10.1016/j.apcatb.2023.123448).

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